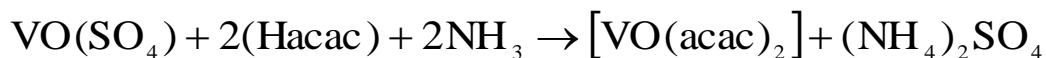


## Synthesis of vanadyl acetylacetonate – Protocol R



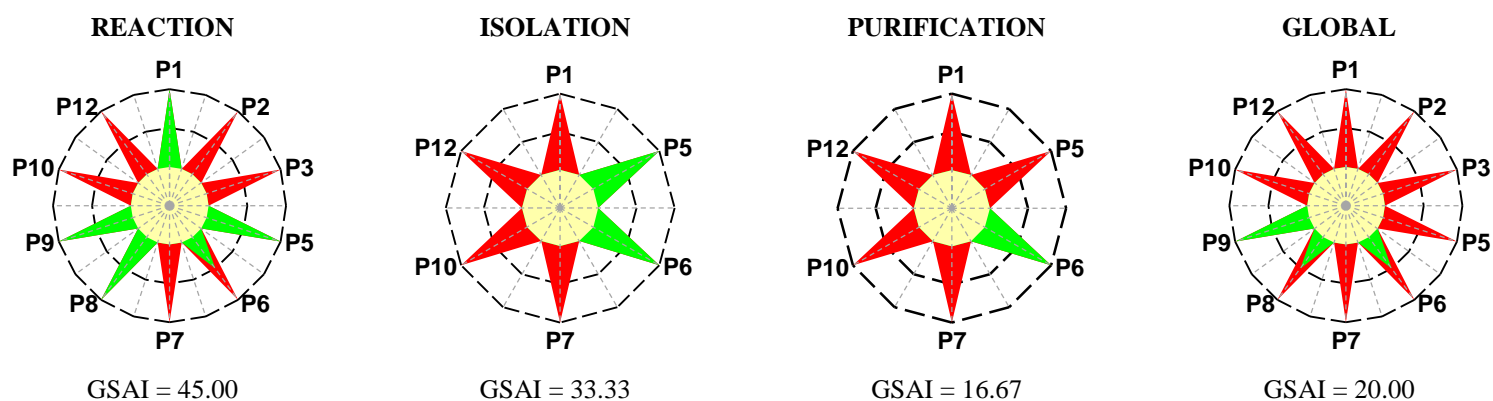
**Reaction.** Mix a solution of 0.01 mol of vanadyl sulphate in water and 6 g (0.058 mol) of acetylacetone (about 190% excess), followed by 20 g (0.333 mol) of urea (about 3230% excess). Cover the reaction mixture with a watch glass and heat overnight on a steam bath. As the urea hydrolyses to release ammonia, the complex separates out.

**Isolation.** Wash the crystals with water and dry in air.

**Purification.** Recrystallize the solid from chloroform.

**Safety.** See hazards associated with the reagents in Table 1.

**Greenness Assessment.** The evaluation was performed using the Green Star (GS) and the results are shown in Figure 1.



**Figure 1.** Greenness assessment (GS) for the synthesis of vanadyl acetylacetonate

## Construction of the GS

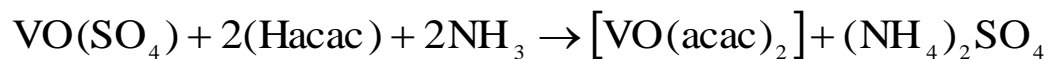
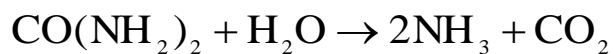


Table 1 presents the hazards and scores associated with the substances involved and Table 2 presents the scores used to construct the green stars.

**Table 1.** Hazards for the synthesis of vanadyl acetylacetonate, protocol R<sup>a</sup>

| Substances involved                       | Step |   |    | Hazard code                              | Score: hazards to... |   |   |
|---|------|---|----|--|----------------------|---|---|
|   | R    | I | Pu |  | HH                   | E | P |
| <b>Stoichiometric reagents</b>            |      |   |    |  |                      |   |   |
| Acetylacetone <sup>c</sup> (CAS 123-54-6) | ✓    |   |    | H226, H302                               | 2                    | 1 | 2 |
| Urea (CAS 57-13-6)                        | ✓    |   |    | -  | 1                    | 1 | 1 |
| Vanadium pentoxide (CAS 1314-62-1)        | ✓    |   |    | H302, H332, H335, H341, H361, H372, H411 | 3                    | 3 | 1 |
| <b>Auxiliary substances</b>               |      |   |    |  |                      |   |   |
| <b>Solvents</b>                           |      |   |    |  |                      |   |   |
| Chloroform (CAS 67-66-3)                  |      |   | ✓  | H302, H315, H351, H373                   | 3                    | 1 | 1 |
| Water <sup>a,b</sup>                      | ✓    | ✓ |    | -  | 1                    | 1 | 1 |
| <b>Product</b>                            |      |   |    |  |                      |   |   |
| Vanadyl acetylacetonate (3153-26-2)       | ✓    | ✓ | ✓  | H302, H315, H319, H335                   | 2                    | 1 | 1 |
| <b>Waste</b>                              |      |   |    |  |                      |   |   |
| Acetylacetone <sup>c</sup> (excess)       |      | ✓ |    | H226, H302                               | 2                    | 1 | 2 |
| Ammonia (excess, solution)                |      | ✓ |    | H315, H318, H400                         | 3                    | 3 | 1 |
| Ammonium sulphate (aqueous solution)      |      | ✓ |    | -  | 1                    | 1 | 1 |
| Carbon dioxide                            | ✓    |   |    | H280                                     | 1                    | 1 | 2 |
| Chloroform                                |      |   | ✓  | H302, H315, H351, H373                   | 3                    | 1 | 1 |
| Water <sup>a,b</sup>                      |      | ✓ |    | -  | 1                    | 1 | 1 |

<sup>a</sup> R – Reaction; I – Isolation; Pu – Purification; HH – Human Health; E – Environment; P – Physical

<sup>a</sup> Renewable; <sup>b</sup> Degradable to innocuous products; <sup>c</sup> Degradable

**Table 2.** Scores used to construct the green star for the synthesis of vanadyl acetylacetonate, protocol R<sup>a</sup>

| Green Chemistry Principle                             | Reaction |   | Isolation |                               | Purification |                           | Global |   |
|---|----------|---|-----------|-------------------------------|--------------|---------------------------|--------|---|
|   | s        | Explanation   | s         | Explanation                   | s            | Explanation               | s      | Explanation   |
| <b>P1</b><br>Prevention                               | 3        | Carbon dioxide  | 1         | Excess of ammonia, H318, H400 | 1            | Chloroform, H351, H373    | 1      | Excess of ammonia, H318, H400, chloroform, H351, H373   |
| <b>P2</b><br>Atom Economy                             | 1        | Excess of reagents > 10%, formation of by-products                            |           | NA                            |              | NA                        | 1      | Excess of reagents > 10%, formation of by-products  |
| <b>P3</b><br>Less hazardous chemical synthesis        | 1        | Vanadium pentoxide, H341, H361, H372, H411, and excess of ammonia, H318, H400 |           | NA                            |              | NA                        | 1      | Vanadium pentoxide, H341, H361, H372, H411, and excess of ammonia, H318, H400, chloroform, H351, H373 |
| <b>P5</b><br>Safer solvents and auxiliary substances  | 3        | Water   | 3         | Water                         | 1            | Chloroform, H351, H373    | 1      | Chloroform, H351, H373  |
| <b>P6</b><br>Increase energy efficiency               | 2        | 0 °C ≤ T ≤ 100 °C   | 3         | Room temperature              | 3            | Room temperature          | 2      | 0 °C ≤ T ≤ 100 °C   |
| <b>P7</b><br>Use renewable feedstocks                 | 1        | Substances not renewable  | 1         | Substances not renewable      | 1            | Substances not renewable  | 1      | Substances not renewable  |
| <b>P8</b><br>Reduce derivatives                       | 3        | One stage   |           | NA                            |              | NA                        | 2      | Two stages  |
| <b>P9</b><br>Catalysts                                | 3        | Without catalysts   |           | NA                            |              | NA                        | 3      | Without catalysts   |
| <b>P10</b><br>Design for degradation                  | 1        | Substances not degradable   | 1         | Substances not degradable     | 1            | Substances not degradable | 1      | Substances not degradable   |
| <b>P12</b><br>Safer chemistry for accident prevention | 1        | Vanadium pentoxide, H341, H361, H372, ammonia, H318                           | 1         | Ammonia, H318                 | 1            | Chloroform, H351, H373    | 1      | Vanadium pentoxide, H341, H361, H372, ammonia, H318, chloroform, H351, H373                           |

<sup>a</sup>s – Score; NA – Not applicable

## References

Mahatma Gandhi University, [http://ietd.inflibnet.ac.in/bitstream/10603/588/14/14\\_chapter9.pdf](http://ietd.inflibnet.ac.in/bitstream/10603/588/14/14_chapter9.pdf) (accessed January 2012).